Microphase separation in two-length-scale multiblock copolymer melts

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Summary

In this thesis the results of a study into the phase behavior of a very special class of so-called multiblock copolymers are reported. Polymer molecules are long molecules consisting of a large number of chemical units, called monomers, that are covalently linked together. The simplest example is a homopolymer consisting of chemically identical monomers together forming a linear chain molecule. Copolymers contain several chemically different monomers that can be linked in many different ways leading to e.g. random copolymers, alternating copolymers, block copolymers, etc. In the melt state chemically different homopolymers usually macrophase separate due to the repulsive exchange interaction between chemically different moieties that is not compensated by the very small entropy of mixing. If two different homopolymers are joint to form a linear diblock copolymer, phase separation will result in a periodic composition modulation with a characteristic length scale. In general the nature of the ordered structures formed will depend on the block copolymer composition as well as the molecular architecture. An example of a non-linear molecular architecture is given by a so-called grafted copolymer. Here side chain molecules are attached to a polymeric backbone. If the side chains are placed at regular distances along the backbone these are also called comb copolymers. Experimental studies on specific comb copolymer-like systems, characterized by two different intrinsic length scales, partly motivated the study presented in this thesis. Experimentally, due to the presence of two length scales, structure-*in*-structure morphologies were observed. From the studies on this specific class of copolymers we adopted

the two-length-scale property, however, to simplify matters somewhat, we restricted ourselves to the linear architecture. Besides this simplification, a new feature was introduced by a further restriction to two chemically different monomers only. As a consequence, the copolymer melts of the general formula A_{fmN}-*b*-$(B_{N/2}$-*b*-$A_{N/2})_n$-*b*-$B_{(1-f)\,mN}$ studied exhibit phase behavior involving a genuine competition between different length scales.

In the introduction the relevant experimental and theoretical results available at the beginning of this study are briefly discussed. In chapter 2 the phase behavior of the compositionally symmetric systems $A_{mN/2}$-*b*-$(B_{N/2}$-*b*-$A_{N/2})_n$-*b*-$B_{mN/2}$ is discussed. We first established the region in the structural parameter n,m space where the scattering function of the system has two maxima, the so-called bifurcation region. The presence of two peaks implies that two different length scales are involved in the thermal composition fluctuations of the system. One length scale is related to the size of the repeat diblock unit of the middle part of the molecule and the other one to the size of the whole macromolecule, both expressed in terms of the corresponding radius of gyration. Depending on the value of the structural parameters one of these length scales determines the periodicity of the structure formed upon cooling. For some values of these parameters, in the vicinity of the so-called equimaxima line, both length scales are important and govern the behaviour of the system upon cooling. In this case structures with two incommensurate periodicities can be formed. We focus on the region of parameters where only one-length-scale (short or long) structures can be formed. This region is very much larger than the region of two-length-scale mesophases, which actually occupies only a very small part of the parameter space. We found that for compositionally symmetric systems several different cubic symmetry phases will be stable, instead of the simple lamellar structure found for the symmetric diblock copolymer. In the weak segregation regime, where the domains of different composition are not well developed yet, e.g. at the first stage of microphase separation, the order-disorder transition is predicted to the following mesophases: lamellar, simple cubic, face-centered cubic and single gyroid, depending on the values of the structural parameters of the macromolecule. In chapter 3 the asymmetry of the end blocks is taking into account. The analysis is again performed in the weak segregation regime. The

double gyroid mesophase, the body-centered cubic and the planar hexagonal phase are found to be stable in addition to the phases present for the symmetric systems.

In the mean-field approximation the fluctuations of the order parameter are neglected. This implies that only the contribution from the density profile, which minimizes the Landau free energy functional, is accounted for and contributions from all other profiles are neglected. For block copolymer melts the elimination of this restriction leads to the replacement of the smooth second order phase transition, predicted by mean-field, by a more or less pronounced first order phase transition. In chapter 4 we discuss the influence of fluctuation corrections on the phase diagrams obtained in chapters 2 and 3. Depending on the values of the structural parameters we distinguished two regimes where the fluctuation corrections are different. One regime corresponds to the regular "multiblock" type, with the short length scale governing the phase behavior. The fluctuation corrections in this regime scale as $\sim 1/N$, with N being the length of the repeat diblock unit. The second regime corresponds to the "triblock" (or "diblock") type, where fluctuation corrections decreases as $\sim 1/N_{tot}$, with N_{tot} being the total length of the macromolecule. Due to the fluctuations, for the asymmetric systems first order phase transitions from the disordered phase into cubic mesophases of different symmetries (body-centered cubic, simple cubic, face-centered cubic, single and double gyroid) are predicted for certain intervals of the structural parameter values.

Inside the bifurcation region where the scattering function has two maxima, we performed the analysis of the fluctuation corrections only on a semi-quantitative level. We considered both maxima independently and compared the free energies, including fluctuations, of the one-length-scale structures formed on either of these length scales. We found that the shift of the phase transition borders for one-length-scale structures due to the fluctuations is determined by a delicate balance between fluctuations on large and small length scales.

In order to extend the results obtained in chapter 2 for larger segregations (lower temperatures) in chapter 5 the self-consistent field theory is applied to investigate the phase behavior of the compositionally symmetric systems. Different solution schemes are discussed and applied for the construction of

various phase diagrams. The pseudo-spectral method in combination with the information about the mesophase symmetry obtained from the weak segregation analysis is found to be more computationally efficient than the spectral or real space method. The results show that upon further cooling first order phase transitions from the large-length-scale cubic phases, predicted by the weak segregation analysis, to other cubic symmetry phases will occur in certain temperature intervals. Starting from the large-length-scale cubic structure upon further cooling a second type of ordering, which involves the formation of lamellar domains inside the middle multiblock part, is expected. Due to the significant computation efforts involved in numerical calculations of the free energies for the three-dimension periodic structures we restricted ourselves to temperatures relatively close to the order-disorder transition temperature, i.e. not very strong segregation. Therefore, we could not predict structure-*in*-structure cubic morphologies, which are expected at lower temperatures. The next step will be to incorporate these into self-consistent field calculations and also to apply the strong segregation theory.